Parity oscillations of Kondo temperature in a single molecule break junction

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We study the Kondo temperature (T_K) of a single molecule break junction. By employing a numerical renormalization group calculations we have found that T_K depends dramatically upon the position of the molecule in the wire formed between the contacts. We show that T_K exhibits strong *oscillations* when the parity of the left and/or right number of atomic sites (N_L, N_R) is changed. For a given set of parameters, the maximum value of T_K occurs for (*odd*, *odd*) combination, while its minimum values is observed for (*even*, *even*). These oscillations are fully understood in terms of the effective hybridization function.

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Kondo effect (KE) is one of the most intriguing phenomena of strong correlated systems,[1] which was beautifully explained by J. Kondo in the 60's in the seminal theoretical work on the minimal resistance in magnetic alloys.[2] KE has revived in the later 90's with the advent of the scanning tunneling microscope (STM) that has facilitated the manipulation of the matter at atomic scale. For instance, STM has allowed observation of interesting facets of the KE in quantum dots (QD)[3] and in single atom or molecule on metallic surfaces,[4–6] which have motivated a huge number of experimental[3,7] and theoretical[8,9] investigations.

One of the experimentally accessible signatures of the KE in nanoscopic system such as QD or magnetic molecules attached to metallic contacts is the strong modification in the conductance across the system, observable when the system is cooled down below the so-called Kondo temperature (T_K). In QD, for instance, T_K is found to be in the sub Kelvin region whereas for large molecules attached to metallic leads T_K can be much larger.[6] In both cases, in the limit of very strong Coulomb interaction, T_K depends strongly upon the effective hybridization (Δ) that connects the localized magnetic moments to the conduction electrons[6,10] as[1] $T_K \sim \exp(\pi\varepsilon_d/\Delta)$, where ε_d (< 0) is the energy of the localized orbital respect to the Fermi level. Controlling Δ or ε_d is therefore crucial for obtaining higher T_K, which is fundamental for possible technological application of KE. While tuning ε_d is relatively simple in QDs by mean of gate voltages, in molecules, on the other hand, it becomes a more complicated task. Conversely, geometrical parameters are more suitably modified in molecules than in QDs and has proven to produce important modifications in T_K via hybridization function.[11]

A suitable experimental arrangement to study the KE is the break junction (BJ) molecular structures, in which a metallic wire (gold wire, for instance) is stretched until a few-atom 1D chain bridges the gap between the electrodes before the complete break up of the wire.[12–16] Owing to the dependence of T_K upon Δ it has been shown that T_K can be mechanically modulated in BJ experiments[11] by changing the distance between the electrodes. Motivated by this experiment, in the present work we study the Kondo temperature of a spin-1/2 magnetic impurity coupled to metallic contacts through two finite (left and right) quantum wires (QW), as illustrated in Fig. 1(a). By employing a numerical renormalization group[17,18] (NRG) calculation we find a strong dependence of T_K upon the parity of the number of sites (N_R, N_L) of each QW as well as their length. The dependence upon the (N_L, N_R) parity combination results in an oscillating behavior of T_K as function of N_L or N_R, akin to what has been observed in Manganese phthalocyanine (MnPc) molecules on top of Pb islands, reported in Ref. 19. Although the system under investigation here is quite different from the one studied in Ref. 19, the origin of the oscillation of T_K can be interpreted likewise. While in their case the enhancement of Δ originates from the formation of multiple quantum well states between the Pb atomic layers, here the enhancement of Δ results from the localized states of the atomic sites of the QW.

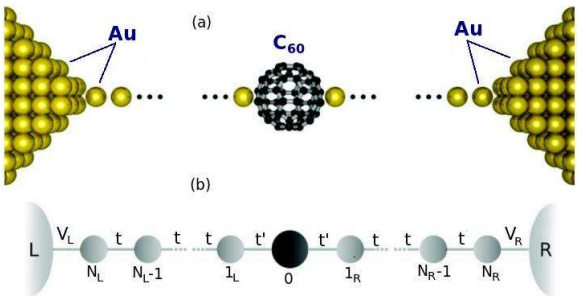

FIG. 1. (Color online) (a) Illustration of a Au quantum wire coupled to metallic contacts with a embedded C_{60} molecule. (b) Pictorial representation of the model. The site labeled as "0" represents the impurity site with strong on-site coulomb repulsion.

Our system model is schematically represented in Fig. 1(b) and is modeled by the Anderson-type Hamiltonian that can be split into five terms as

$$H = H_{imp} + H_{cb} + H_{wires} + H_{imp-wires} + H_{cbs-wires}, \quad (1)$$

where H_{imp}, H_{cb} and H_{wires} describe, respectively, the interacting impurity, the free electrons in the conduction bands and the electrons in the wires, $H_{imp-wires}$ couples the impurity to the two wires and $H_{cb-wires}$ couples the wires the their respective conduction bands. In terms of creation and annihilation

fermion operators the Hamiltonians read

$$H_{imp} = \sum_{\sigma} \varepsilon_d c^{\dagger}_{d\sigma} c_{d\sigma} + U n_{d\uparrow} n_{d\downarrow}, \quad (2)$$

$$H_{cb} = \sum_{\ell=R,L} \sum_{k\sigma} \varepsilon_k c^{\dagger}_{\ell k\sigma} c_{\ell k\sigma} \quad (3)$$

$$H_{wires} = \sum_{\ell=R,L} \left[\varepsilon_0 \sum_{\substack{i_\ell=1 \\ \sigma}}^{N_\ell} n_{i_\ell\sigma} + t \sum_{\substack{i_\ell=1 \\ \sigma}}^{N_\ell - 1} \left(c^{\dagger}_{i_\ell\sigma} c_{i_\ell+1} + H.c. \right) \right], \quad (4)$$

$$H_{cb-wires} = \sum_{\ell=R,L} \sum_{\ell k\sigma} \left(V_{\ell k} c^{\dagger}_{N_\ell} c_{\ell k\sigma} + V^{*}_{\ell k} c^{\dagger}_{\ell k\sigma} c_{N_\ell} \right) \quad (5)$$

$$H_{imp-wires} = t' \sum_{\ell=R,L} \sum_{\ell\sigma} \left(c^{\dagger}_{d\sigma} c_{1_\ell} + c^{\dagger}_{1_\ell\sigma} c_{d\sigma} \right). \quad (6)$$

In Eqs. 2-6, the operators $c^{\dagger}_{d\sigma}$ ($c_{d\sigma}$) creates (annihilates) an electron in the orbital d with energy ε_d, $c^{\dagger}_{\ell k\sigma}$ ($c_{\ell k\sigma}$) creates (annihilates) an electron in the ℓth conduction band with energy ε_k, $c^{\dagger}_{i_\ell\sigma}$ ($c_{i_\ell\sigma}$) creates (annihilates) and electron in the ith site of the ℓth QW with energy ε_0 spin σ. Finally, t is the hopping between two adjacent sites in the wires and $V_{\ell k}$ and t' couple the QWs to their conduction bands and to the impurity, respectively. The conduction bands are characterized by a flat density of states, $\rho(\omega) = (1/2D)\Theta(D - |\omega|)$, where D is their half bandwidth and $\Theta(x)$ is the Heaviside step function. It is worth emphasizing that although the motivating experiment was realized using C_{60} molecule coupled to Au metallic contacts, this model is rather general. In the particular context of molecular BJ, vibrations may be important in certain range of parameters, but this aspect is beyond the scope of the present work.

In order to properly address the Kondo physics of the system, the full Hamiltonian is approached by using the numerical renormalization method, with which we can calculate the thermodynamical properties. Within the NRG approach we discretize the effective conduction band "seen" by the interacting impurity. The effective conduction band can be determined by exact calculation of the local non-interacting ($U = 0$) Green's function (suppressing the spin index), $g_{dd}(\omega) = [\omega - \epsilon_d + \Sigma(\omega)]^{-1}$, where $\Sigma = \Sigma_R(\omega) + \Sigma_L(\omega)$, in which the ℓth self-energy is given by

$$\Sigma_\ell(\omega) = -\cfrac{t'^2}{\omega - \cfrac{t^2}{\omega - \cfrac{t^2}{\omega - \cfrac{t^2}{\omega - \cfrac{\ddots\, t^2}{\omega - V^2_\ell \tilde{g}(\omega)}}}}}, \quad (7)$$

with

$$\tilde{g}(\omega) = -\frac{1}{2D} \ln \left| \frac{\omega - D}{\omega + D} \right| - \frac{i\pi}{2D} \Theta(D - |\omega|) \quad (8)$$

being the diagonal GF associated to the unperturbed conduction electrons in the leads. The fraction in Eq. 7 is continued until all the sites of the of the ℓth wire and the ℓth conduction band are taken into account.

The hybridization of the localized orbital "d" with the effective band is give by $\Delta(\omega) = \mathrm{Im}[\Sigma(\omega)] = \Delta_L(\omega) + \Delta_R(\omega)$ [Hereafter we will refers to $\Delta(0)$ just as Δ]. The hybridization function is logarithmically discretized[18,20] to map the system in a Wilson's chain form,[17]

$$H = H_{imp} + t' \sum_{\sigma} \left(c^{\dagger}_{d\sigma} c_{0\sigma} + c^{\dagger}_{0\sigma} c_{d\sigma} \right) + \sum_{\substack{i=0 \\ \sigma}}^{\infty} \varepsilon_{i\sigma} c^{\dagger}_{i\sigma} c_{i\sigma} + \sum_{\substack{i=0 \\ \sigma}}^{\infty} t_i \left(c^{\dagger}_{i\sigma} c_{i+1\sigma} + c^{\dagger}_{i+1\sigma} c_{i\sigma} \right), \quad (9)$$

where t_i's are calculated via $\Delta(\omega)$, following the recipes described in Ref. 20. Once we have mapped the system in the Wilson's form, we proceed the NRG calculation, which is based in the iterative diagonalization of the effective Hamiltonian.[18] After reaching the strong coupling fixed point we can calculate the magnetic moment within the canonical ensemble as

$$k_B T \chi(T) = \frac{1}{Z(T)} \sum_{\nu} \left[\langle \nu | S^2_z | \nu \rangle - (\nu | S_z | \nu \rangle)^2 \right] e^{-E_\nu / k_B T}, \quad (10)$$

where k_B is the Boltzmann constant, $Z(T) = \sum_\nu \exp(-E_\nu / k_B T)$ is the canonical partition function, S_z is the spin operator, $|\nu\rangle$ and E_ν are, respectively, the eigenvector and its corresponding eigenvalue of the full interacting Hamiltonian, which are naturally calculated in the NRG procedure.[21] Following Wilson's criterion, we define T_K from the "impurity" magnetic moment as $k_B T_K \chi_{imp}(T_K) = 0.0707(g\mu_B)^2$, (that is the magnetic moment of the full system subtracted by the contribution of the effective conduction band), g is the electron g-factor and μ_B is the Bohr magneton.

Before starting the presentation of our numerical results, lets analyze the hybridization function at the Fermi level, which is the most relevant parameter to determine the behavior of T_K in our calculations. It is straightforward to show from Eq. 7 that Δ possesses only three distinct vales,

$$\Delta = \begin{cases} \Delta_{min} = \Delta_0 & \text{for (even,even)} \\ \Delta_{int} = \Delta_0 \left(\frac{1}{2} + \alpha \right) & \text{for (even,odd) or (odd,even)} \\ \Delta_{max} = 2\alpha\Delta_0 & \text{for (odd,odd)} \end{cases}, \quad (11)$$

where we have defined $\Delta_0 = \pi t'^2 / D$ and denoted Δ_{min}, Δ_{int} and Δ_{max}, the minimum, intermediate and maximum value of Δ, respectively, and $\alpha = 2(D/\pi t)^2$ is a dimensionless parameter that can be modified, for instance, by stretching the QW as is was done in the Ref. 11. To obtain our numerical results lets set $D = 1$ as our energy scale. With that we choose hereafter (unless otherwise stated) $U = 0.5$, $\epsilon_d = -0.25$, $\varepsilon_0 = 0$ (at the particle-hole symmetric point), $V_R = V_L = t = 0.15$ and $t' = 0.1$.

In Fig. 2 we show the hybridization function vs energy for various values of N_L and N_R. In Figs. 2(a), 2(b), and 2(c) we fix $N_L = 0$ and show $\Delta(\omega)$ for $N_R = 1$, $N_R = 2$ and $N_R = 3$, while in Figs. 2(d), 2(e), and 2(f) we keep $N_L = 1$ fixed and show $\Delta(\omega)$ for $N_R = 2$, $N_R = 3$ and $N_R = 4$. The number of peaks of $\Delta(\omega)$ is given by $\max(N_L, N_R)$ for equal parity and

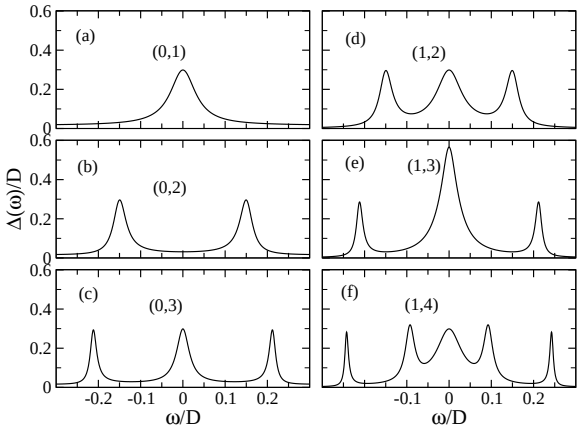

FIG. 2. (Color online) Hybridization function vs energy for various values of N_L and N_L [denoted in the figure as (N_L, N_R) using $V_L = V_R = t = 0.15$ and $t' = 0.1$. Notice that Δ possesses three different values, depending on the parity of N_L and N_R. The minimum (Δ_{min}) and maximum (Δ_{max}) value of Δ is obtained for $(even, even)$ (b) and (odd, odd) (e), respectively, while for all the other combinations Δ has an intermediate value, Δ_{int}.

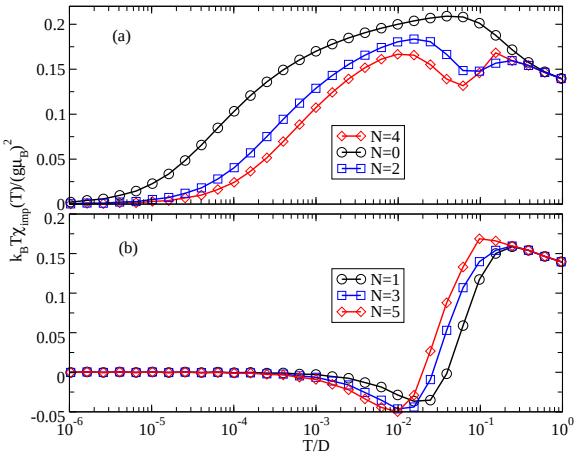

FIG. 3. (Color online) Magnetic moment as function of temperature for various values of $N_R = N_L = N$. Panel (a) and (b) correspond to N even and odd, respectively (see values of N in the legends).

$N_R + N_L$ for different parities. Although the structure of $\Delta(\omega)$ away from the Fermi level has some effect on T_K, the most relevant contribution comes from the structures *at* or *very close* the the Fermi level. For the parameters set above, we obtain $\Delta_{min} \approx 0.0314$, $\Delta_{max} \approx 0.566$ and $\Delta_{int} \approx 0.299$. These distinct values of Δ are crucial for determining the Kondo temperature of the system, which in our case can be roughly estimated as[22] $k_B T_K(\Delta) \sim \exp[-\pi U/8\Delta]$. It is clear that T_K increases as Δ increases.

In Fig. 3(a) and Fig. 3(b) we show the magnetic moment as function temperature for various values of $N = N_L = N_R$ (the symmetric case) even and odd, respectively. The case of $N = 0$ [Fig. 3(a), ○ (black)] corresponds to the single impurity coupled to two conduction band. The low temperature suppression in the magnetic moment results from the Kondo

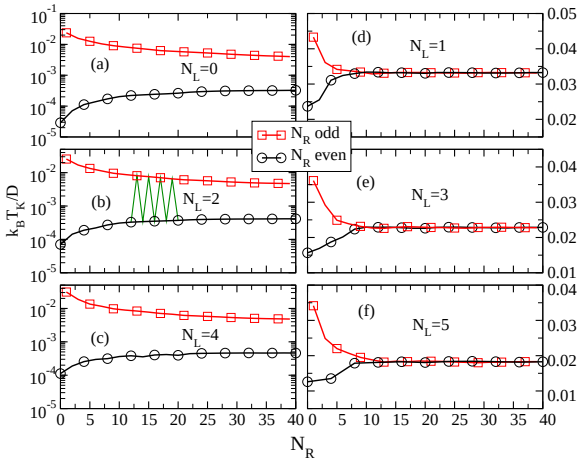

FIG. 4. (Color online) Kondo temperature as function of number of sites (N_R) for a fixed $N_L = 1$. ○ (black) and □ (red) correspond to even (odd) N_R, respectively. The zig-zag (green) line shows the $(even, odd)$ oscillation, similar to those observed in Ref. 19.

screening of the local spin [these curves are used to T_K, as discussed above]. On the other hand, in the high temperature limit the $k_B T\chi \to (g\mu_B)^2/8$, as expected. Notice in Fig. 3(a) that T_K increases when N (even) increases. Conversely, T_K decreases when N (odd) increases as seen in Fig. 3(b). Notice also that T_K can be at least two order of magnitude larger for N odd than for N even. This huge difference will be analyze below. The result for $N = 1$ [Fig. 3(b), ○ (black)] is equivalent to those reported in Ref. 10. The negative values of $k_B T\chi_{imp}$ within a small range of T results from the subtraction of the effective conduction band contribution.

In order to show the behavior of the Kondo temperature for larger and different values of N_L and N_R we show in Fig. 4 T_K as function of N_R for a fixed number N_L even (left) and N_L odd (right). The ○ (black) curves correspond to N_R even, while □ (red) curves corresponds to N_R odd. Notice that for N_L even [(Fig. 4(a), 4(b) and 4(c)] T_K increases with N_R even [○ (black)] while it decreases for N_R odd [□ (red)]. Observe again that for small N_R T_K is almost two order of magnitude larger for N_R odd than for N_R even (keeping N_L even). This difference decreases asymptotically for large N_R and vanishes asymptotically as $N \to \infty$. This results from the fact that in this situation the conduction electrons near the Fermi level are more strongly coupled to the impurity, reflecting the fact that Δ_{int} is larger than Δ_{min} as clearly shown in Fig. 2. For N_L odd (Fig. 2(d), 2(e) and 2(f) we observe a similar behavior (T_K increases as N_R even increases and decreases as N_R even increases) but in this case the curves collapse onto each other very quickly (typically for $N_R = 10$) to a larger value, when compared to the case of N_L even. At least for small N_L and N_R we can roughly estimate the ratio between T_K's for the three distinct values of Δ as

$$\frac{T_K(\Delta_a)}{T_K(\Delta_b)} = e^{\frac{\pi U}{8}\left(\frac{\Delta_a - \Delta_b}{\Delta_a \Delta_b}\right)}, \qquad (12)$$

where a and b stand for *min*, *int* and *max*. Using the parameters chosen above we obtain $T_K(\Delta_{int})/T_K(\Delta_{min}) \approx 2.7 \times 10^2$,

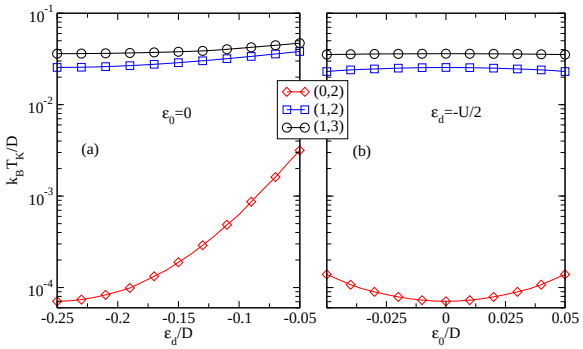

FIG. 5. (Color online) Kondo temperature as function of ε_d ($\varepsilon_0 = 0$) (a) and ε_0 ($\varepsilon_d = -U/2$) (b) for various configuration of (N_L, N_R) as shown in the legend. The other parameter are the same as in the previous figures.

while $T_K(\Delta_{max})/T_K(\Delta_{int}) \approx 1.36$. These values are consistent with the huge difference between the values shown in □ (red) and ○ (black) curves of Figs. 4(a), 4(b) and 4(c) and small difference in the related curves of Figs. 4(d), 4(e) and 4(f). The behavior of T_K with increasing N_L and N_R for the same parity combination cannot be explained in terms of Δ. This can be reasonably understood in terms of the formation of a small sub-band inside the conduction band, due to a large number of atomic sites and the energy dependence of hybridization function near the Fermi level. In the limit of $N_L, N_R \to \infty$ the sub-band becomes a smooth curve, resulting in a T_K independent of the lengths of the wires. The zig-zag (green) line in Fig. 4(b) shows the even-odd oscillations in T_K, very similar to what was observed in Ref. 19. Finally, in Fig. 5 we show the robustness of these results against particle-hole symmetry breaking. In Fig. 5(a) show T_K as function of ε_d for $\varepsilon_0 = 0$. Notice that, although more pronounced for the $(even, even)$ case, T_K increases as ε_d is shifted upward from $-U/2$ for all parities [(0,2), (1,2) and (1,3)]. Same behavior is obtained for the other side (not shown). These are consistent with the general expression,[23] $T_K \sim Exp[-\pi|\varepsilon_d|(\varepsilon_d + U)/(2\Delta U)]$ for constant hybridization function. When we keep ε_d and vary ε_0 about the Fermi level [Fig. 5(b)] we see that T_K increases for $(0, 2)$ but decrease slightly for $(1, 2)$ and $(1, 3)$. This results from the fact that, as ε_0 deviates from the Fermi level, $\Delta(0)$ decreases if $\Delta(\omega)$ possesses a peak at the Fermi level as in the $(even, odd)$, $(odd, even)$ or (odd, odd) cases, but increases when $\Delta(\omega)$ exhibits a dip at the Fermi level as in the $(even, even)$ configuration.

In conclusion, we have presented a detailed study of the Kondo temperature of a single molecule break junction. By employing a numerical renormalization group we show that T_K is strongly dependent of the parity of the number of atomic sites in each piece of QW connecting the molecule to the contacts. More interesting, we show that the T_K oscillates when the parity of the number of sites of the wires changes. These oscillations are interpreted in terms of the effective hybridization function $\Delta(\omega)$. For $(even, even)$ and (odd, odd) configurations the effective coupling Δ is minimum and maximum, respectively, while for $(even, odd)$ or $(odd, even)$ configurations Δ possesses an intermediate value. Within this picture, the huge variation of T_K is readily estimated by a simple analytical calculation, which can vary up to a factor of 10^2 [in the case of changing from $(even, even)$ to $(even, odd)$]. Our results provide a very clear picture of the main ingredient responsible for the dramatic dependence of T_K on geometrical configuration of single molecule break junctions as well as of magnetic molecule on atomic layer surfaces. Moreover, we believe our results can be used to guide experimental realizations of high-T_K experiments.

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